

Dissociative Photoionization of Methyl Thiochloroformate, ClC(O)SCH_3 , Following Sulfur 2p, Chlorine 2p, Carbon 1s, and Oxygen 1s Excitations

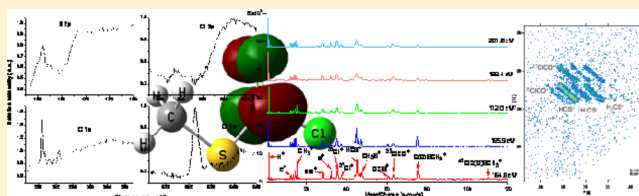
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ABSTRACT: The electronic transitions and the dissociative ionic photoionization mechanisms of gaseous ClC(O)SCH_3 have been investigated at the VUV and soft X-ray energy regions of S 2p, Cl 2p, C 1s, and O 1s core edges using tunable synchrotron radiation and time-of-flight mass spectrometry. The relative abundances of the ionic fragments were obtained from both PEPICO (photoelectron photoion coincidence) and PEPIPO (photoelectron photoion photoion coincidence) spectra. The presence of a moderate site- and element-specific fragmentation effects and its implication regarding chemical reactions were analyzed. The relationship of the current results with the interstellar chemistry is also a goal of this piece of work.



INTRODUCTION

As a general project aimed to elucidating the shallow and inner-shell core electronic properties of carbonylsulfonyl derivatives, XC(O)SY , and hence gaining a fuller understanding of the photodissociation channels open to these compounds, our research group have carried out photoionization studies on species such as FC(O)SCI , ClC(O)SCI , $\text{CH}_3\text{C(O)SH}$, $\text{CH}_3\text{OC(O)SCI}$, FC(O)SCH_3 , $\text{ClC(O)SCH}_2\text{CH}_3$, and $\text{CH}_3\text{C(O)SCH}_3$ using synchrotron radiation in the range of 100–1000 eV.^{1–8} These studies involved measurements of not only the total ion yield (TIY) and partial ion yield (PIY) spectra but also multicoincidence spectra [photoelectron photoion coincidence (PEPICO) and photoelectron photoion photoion coincidence (PEPIPO)] around the main ionization edges. The study of photoionization processes for the carbonylsulfonyl compounds was also extended to the valence region.^{7,9–11} The combination of photoelectron spectroscopy PES and multicoincidence time-of-flight (TOF) based techniques seems to offer a most promising approach to a deeper understanding of the electronic structure and the ionic dissociation induced by photon absorption in the valence region.

In the present work, we report a study of the photon impact excitation and ionization dissociation dynamics on another member of the carbonylsulfonyl family, namely, methyl thiochloroformate ClC(O)SCH_3 . In a previous work, the title molecule was investigated by our group using results from both PES and synchrotron radiation in the valence energy range.¹¹ In an additional series of experiments, total ion yield (TIY) and

PEPICO spectra were recorded in the 12.0–21.5 eV energy range. Vibronic structure has been observed in the TIY spectrum recorded in the synchrotron experiments. In addition, it was found that the relative abundances of the photodissociation products of ClC(O)SCH_3 strongly depend on the excitation radiation in the valence energy range. Thus, for several ionization energies, including off-resonance values, the signal of the COSCH_3^+ ion was the most intense in the spectra. Another set of spectra, excited with photon energies corresponding to the most prominent maxima of the TIY spectrum, were dominated by the CS^+ fragment, whereas OCS^+ is the most abundant positive ion when the sample was irradiated with 15.45, 15.60, and 15.76 eV, and S^+ is the most abundant positive ion at 16.44 and 16.59 eV. A very remarkable result was found with photons of 15.90 eV for which the most intense signal corresponds to HCl^+ .

One of the goals of the present study is to obtain evidence regarding the electronic transitions throughout the whole region of the S 2p, Cl 2p, C 1s, and O 1s core edges as well as the ionic dissociation mechanisms following the electronic relaxation of the core excited methyl thiochloroformate. The methodology includes the use of tunable synchrotron radiation and multicoincidence TOF-mass spectroscopy techniques. Thus, fragmentation patterns deduced from PEPICO spectra

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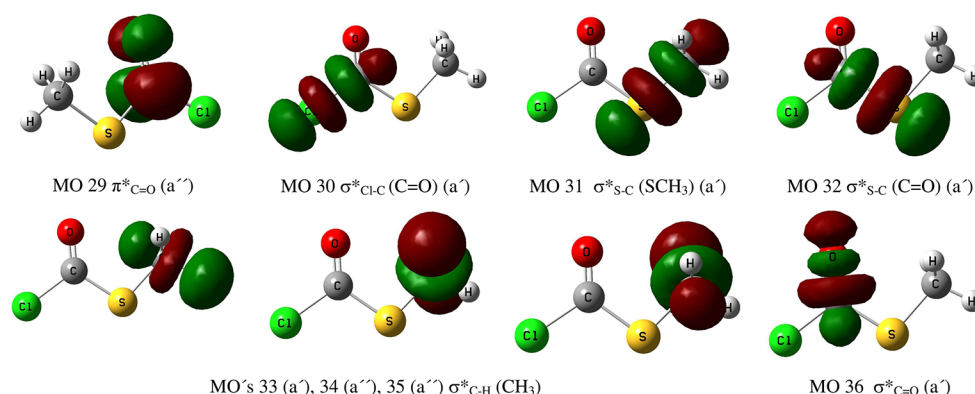


Figure 1. Characters of the eight lower energy unoccupied molecular orbitals for ClC(O)SCH_3 calculated at the B3LYP/6-311++G (d,p) level of approximation.

at various excitation energies in the VUV and soft X-ray regions were especially analyzed in order to establish the existence of a site- and element-specific fragmentation effects.^{12,13}

In fact, differences in relative yields of fragment ions were observed in simple molecules by exciting K shell electrons.¹⁴ The tunable synchrotron radiation can excite selectively inner shell electrons, and in a case where the memory effect induced on the short time scale of the excitation is conserved at longer times than that required for the ionic dissociation, nonstatistical fragmentations, i.e., site- and element-specific fragmentations, can be anticipated. The insight on the nature of the site specific fragmentation is of importance in understanding localization phenomena in chemical reactions.^{15–18} With reference to the photofragmentation dynamics of both halogencarbonylsulfonyl chlorides, XC(O)SCl ($\text{X} = \text{F}, \text{Cl}$), the branching ratios for ion productions obtained from the PEPICO spectra exhibit only small changes with the incident photon energy, which was interpreted in terms of a lose memory effect or nonspecific fragmentation after an Auger decay, promoted by the delocalization of valence orbitals over the whole planar molecules.^{1–3} However, in a similar experimental study carried out for $\text{CH}_3\text{C(O)SH}$, $\text{CH}_3\text{OC(O)SCl}$, FC(O)SCH_3 , and $\text{CH}_3\text{C(O)SCH}_3$, a moderate site-specific fragmentation was observed.^{4–6,8} Moreover, we recently demonstrated the presence of site-specific fragmentation when the fluorinated species FC(O)SCH_3 is irradiated at the S 2p and F 1s absorption edges.⁶

The elucidation of the ionic dissociation mechanisms is another goal for the present work, thus, ionic double coincidences were examined in the present work for the title molecule and dissociation mechanisms were proposed to explain the shape and slope of observed PEPICO islands. The relationship of the current results with the interstellar chemistry is also a subject of discussion in the present article.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Synchrotron radiation was used at the Laboratório Nacional de Luz Síncrotron (LNLS), Barão Geraldo, Campinas, São Paulo, Brazil.^{19–21} Linearly polarized light monochromatized through a toroidal grating monochromator (available at the TGM beamline in the range 12–300 eV),^{22,23} with resolving power of $\Delta E/E < 400$, to excite the region of S 2p and Cl 2p, and a spherical grating monochromator (available at the SGM beamline in the range 200–1000 eV)²⁴ with $\Delta E/E < 200$, to excite the region of C 1s and O 1s, intersects the effusive

gaseous sample inside a high vacuum chamber, with base pressure in the range 10^{-8} mbar. During the experiments, the pressure of the sample was maintained below 2×10^{-6} mbar. The intensity of the emergent photon beam was recorded with a light-sensitive diode. The ions produced by the interaction of the gaseous sample with the light beam were detected using a TOF mass spectrometer of the Wiley–McLaren type for both PEPICO and PEPIPICO measurements.^{25–27} This instrument was constructed at the Institute of Physics, Brasilia University, Brasilia, Brazil.²⁸ The axis of the TOF spectrometer is perpendicular to the photon beam and parallel to the plane of the storage ring. Electrons are accelerated to a multichannel plate (MCP) and recorded without energy analysis. This event starts the flight time determination process of the corresponding ion, which is consequently accelerated to another MCP.

The sample of ClC(O)SCH_3 was obtained from a commercial source (Aldrich, estimate purity better than 95%). The liquid was purified by repeated trap-to-trap condensations at reduced pressure in order to eliminate volatile impurities. The purity of the compound in both the vapor and the liquid phases was carefully checked by gas IR and liquid Raman spectroscopy.^{29,30}

Theoretical calculations have been computed with the three-parameter density functional (B3LYP), which includes Becke's gradient exchange correction³¹ and the Lee, Young, and Parr correlation functional³² using standard 6-311++G(d,p) basis set^{33,34} and the Gaussian03 program package.³⁵

RESULTS AND DISCUSSION

Theoretical Calculations. It is well-established that the ClC(O)SCH_3 molecule in its electronic ground state belongs to the C_s symmetry point group. It follows that all canonical molecular orbitals of type a' are σ -orbitals lying in the molecular plane, while those of type a'' are π -orbitals.¹¹ Accordingly, in the ground state electronic configuration of methyl thiochloroformate, the 30 valence electrons are then arranged in 15 double-occupied Kohn–Sham orbitals in the independent particle description.

Quantum chemical calculations at the UB3LYP/6-311++G (d, p) level of approximation using the Gaussian03 program package³⁵ were performed in the previous article¹¹ to analyze the nature of the cation formed in the first ionization process. Thus, the calculated value of the adiabatic ionization potential (IP) was 9.80 eV. The heavy-atom planar skeleton of the ClC(O)SCH_3 molecule remains unchanged after simple ionization with a remarkable elongation of about 0.23 Å of

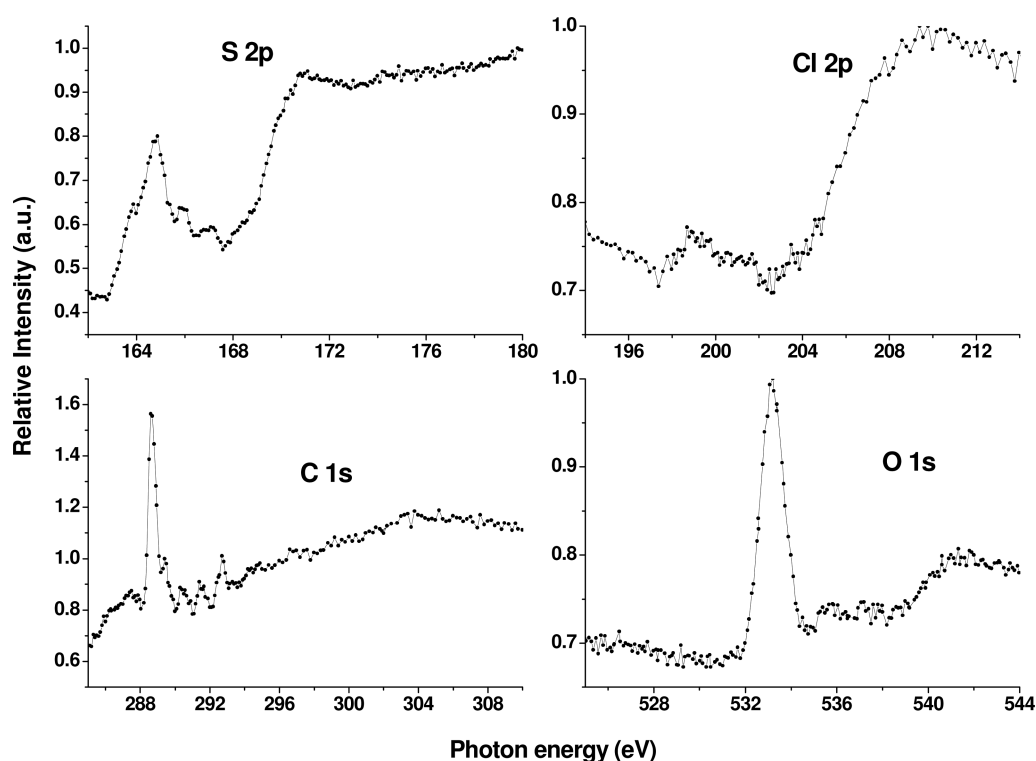


Figure 2. TIIY spectra of ClC(O)SCH₃ in the S 2p, Cl 2p, C 1s, and O 1s regions.

the C–S bond involving the carbonyl carbon atom and the shortening of the other bond lengths. The bond angles are quite similar to those calculated for the neutral species. Furthermore, the *syn* orientation of the C=O with respect to the S–C opposite bond is retained after ionization. However, according to the UB3LYP/6-311++G(d, p) method, the doubly charged state is located at 25.8 eV above the neutral ground state. When this species is compared with the neutral form, huge differences are observed in bond distances, bond angles, and torsions. Thus, the ClC–SC dihedral angle changes from 180° in *syn*-ClC(O)SCH₃ to 89° in ClC(O)SCH₃²⁺ (nearly gauche orientation). This behavior resembles our former studies on this family of carbonylsulfenyl compounds.^{1,3–6,8}

To determine the valence type vacant orbitals, quantum chemical calculations at the B3LYP/6-311++G(d, p) level of approximation for neutral ClC(O)SCH₃ in its ground state were performed. The LUMO is a $\pi^*_{\text{C=O}}$ (a'') orbital with antibonding character (see Figure 1). The next vacant orbitals correspond to the antibonding $\sigma^*_{\text{Cl-C}}$ (C=O) (a'), followed by the two C–S antibonding orbitals [$\sigma^*_{\text{S-C}}$ (SCH₃) (a') and $\sigma^*_{\text{S-C}}$ (C=O) (a')]. Three antibonding orbitals with similar energies attributed as $\sigma^*_{\text{C-H}}$ localized in the CH₃ group and a $\sigma^*_{\text{C=O}}$ (a') complete the antibonding molecular orbital representation expected for ClC(O)SCH₃.

Total Ion Yield Spectra (TIY). The TIY spectra have been obtained by recording the count rates of the total ions, while the photon energy is scanned. At high photon energies corresponding to shallow- and core-shell electronic levels, the quantum yield for molecular ionization is quite likely tending to unity. Consequently, the detection of parent and fragment ions as a function of the incident photon energy is a powerful method to be used as a complement to the absorption spectroscopy.³⁶ The TIY spectrum of ClC(O)SCH₃, measured near the S 2p edge, is shown in Figure 2. The tentative assignments of the principal bands observed in the TIY spectra

measured in this work were made assisted by the computed unoccupied orbitals and by comparison with examples of the literature.^{1–11}

Below the S 2p threshold (approximately 171.0 eV), the spectrum is dominated by an intense resonance located at 164.8 eV, and below and above this photon energy, other low intense bands can be observed at around 165.9, 167.1, and 163.8 eV. Furthermore, it is expected that a spin–orbital split occurs in the excited species for the 2p term of sulfur atom in 2p_{1/2} and 2p_{3/2} levels, and in agreement with the 2J + 1 rule, an intensity ratio of 1:2 is expected for these transitions. For the simplest sulphide molecule, H₂S, a similar transition splitting of 1.201 eV has been reported.³⁷ In the present case, the splitting between the two most intense signals is 1.1 eV. The features observed in the TIY spectrum recorded in the S 2p region compare very well with previous data obtained for the related molecule ClC(O)SCH₂CH₃, recently examined.⁷ Thus, in a similar way, the first resonances at 164.8 and 165.9 eV could be tentatively assigned to the S 2p → $\pi^*_{\text{C=O}}$ transition. For the title molecule and also for the ClC(O)SCH₂CH₃ species, the expected intensity ratio of 1:2 for the 2p_{1/2} and 2p_{3/2} levels has not been observed, suggesting the presence of overlapping transitions.⁷ In addition, as in the case of ClC(O)SCH₂CH₃, the $\sigma^*_{\text{C=O}}$ antibonding orbital was computed as a high-energy vacant orbital, corresponding to the LUMO + 7 (see Figure 1). Therefore, the S 2p → $\sigma^*_{\text{C=O}}$ transition is expected to appear near the S 2p ionization edge. This fact is in agreement with the inner-shell excitation spectra of carbonate species, which show a significant energy separation between transitions involving both $\pi^*_{\text{C=O}}$ and $\sigma^*_{\text{C=O}}$ orbitals.³⁸

In the TIY spectrum measured near the Cl 2p region (Figure 2), the threshold is located at approximately 209.0 eV, and below this photon energy, two broad and poor resolved signals can be observed at 199.4 and 201.6 eV. The observed resonance transitions may be mainly assigned to transitions

involving the spin–orbit split of the 2p term in the $2p_{1/2}$ and $2p_{3/2}$ levels of the excited chlorine species toward the unoccupied $\sigma^*_{\text{Cl-C}}$ antibonding orbital.³⁹ A similar assignment was reported for the other chlorinated species formerly studied.^{7,40}

In the TIY spectrum obtained near the C 1s region (Figure 2), the C 1s threshold is located at approximately 298.0 eV, and below this photon energy, an intense signal at around 288.7 eV can be observed together with other low intense bands. Although two nonequivalent carbon atoms are present in ClC(O)SCH_3 , we were not able to assign the spectra from these different excitation sites. As mentioned before, the lowest unoccupied orbital (LUMO) in ClC(O)SCH_3 is a π^* orbital residing primarily at the carbonyl carbon and oxygen sites. Thus, it is expected that an intense $1s-\pi^*$ transition from the carbonyl carbon and the oxygen site would be observed. The most intense signal observed in this energy range may be associated with the excitation of the 1s C (C=O) toward the vacant π^* antibonding orbital because the carbon atoms of saturated hydrocarbons show mainly Rydberg transitions being that their intensities are in general 1 order of magnitude lower than those related to excitations to $\pi^*_{\text{C=O}}$ antibonding orbitals.⁴¹ The features observed in the TIY spectrum of the title species are similar to those previously reported for the related FC(O)SCH_3 molecule, recently analyzed in our group. A parallel assignment of the absorptions was performed for both species.⁶

The TIY spectrum obtained near the O 1s region (Figure 2) is dominated by an intense resonance centered at 532.9 eV, whereas the O 1s threshold is located at approximately 540.0 eV. A low-intensity signal was also observed at 535.6 eV. As has been reported for other carbonyl compounds,³⁸ electronic excitations to vacant antibonding $\pi^*_{\text{C=O}}$ and $\sigma^*_{\text{C=O}}$ orbitals may be associated with the signals observed at 532.9 and 535.6 eV, respectively. Moreover, for the O 1s spectra of FC(O)SCH_3 , which is closely related to the title molecule because they are isoelectronic species, two resonances were observed at 528.5 ($\text{O } 1s \rightarrow \pi^*_{\text{C=O}}$) and 531.9 ($\text{O } 1s \rightarrow \sigma^*_{\text{C=O}}$) eV, and the ionization potential was estimated at 535.7 eV.¹ Thus, very similar term values are found, giving confidence to the proposed assignment.

PEPICO Spectra. Several PEPICO spectra that include the photon energies corresponding to the most important S 2p, Cl 2p, C 1s, and O 1s transitions of ClC(O)SCH_3 have been recorded. In order to identify the role of resonant processes in the fragmentation, the spectra were also measured at photon energy values below (typically 10 eV) and above (typically 50 eV) the ionization edges. For all spectra, the intensity of each ionic fragment is obtained as the integrated area under the peak, fitted as Gaussian functions. The spectra correspond to the arrival of only one ion during the open time window. They, therefore, contain both contributions of a single ionization and multiple ionization processes where only the lighter ion can be detected.

The PEPICO spectra taken at representative photon energies near the S 2p and Cl 2p and C 1s and O 1s edge absorptions of ClC(O)SCH_3 are shown in Figures 3 and 4, respectively. In Table 1, the corresponding branching ratios are gathered for the main fragment ions.

Naturally occurring isotopomer fragments, mainly due to the presence of ^{35}Cl and ^{37}Cl isotopes, are clearly observed due to the suitable mass resolution attained in the experiments. This

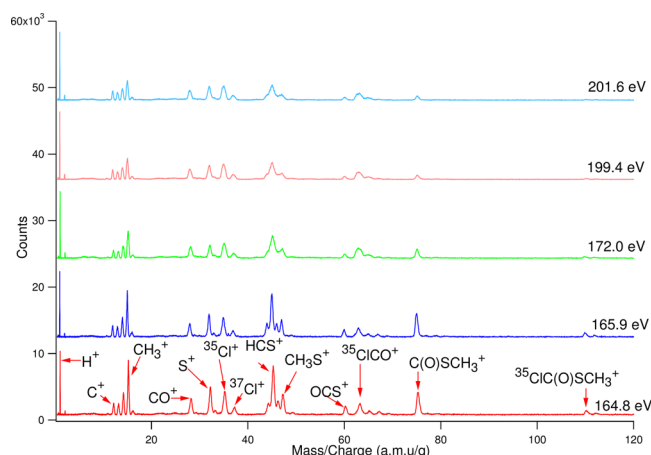


Figure 3. PEPICO spectra measured for ClC(O)SCH_3 at selected photon energies around the S 2p and Cl 2p edge absorptions.

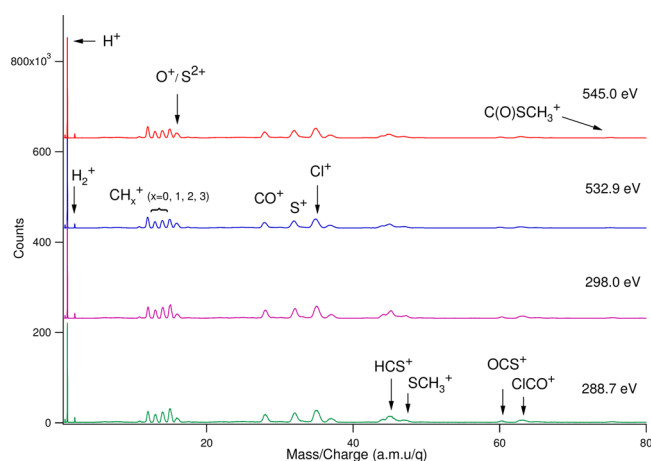


Figure 4. PEPICO spectra measured for ClC(O)SCH_3 at selected photon energies around the C 1s and O 1s edge absorptions.

fact assists the assignment of the ion fragments appearing in the coincidence spectra.

The most intense peak for the S 2p energy range is observed for the HCS^+ ($m/z = 45$) ion with relative intensities between 9.0 and 12.0%. The next most abundant ions are CH_3^+ ($m/z = 15$), Cl^+ ($m/z = 35$), and H^+ ($m/z = 1$) reaching branching values of 9.2, 7.9, and 8.8%, respectively. Signals for the CO^+ ($m/z = 28$) and S^+ ($m/z = 32$) ions can be observed in this energy range, showing relative abundances of the order of about 6%.

The group of CH_x^+ fragments ($x = 0, 1, 2$), whose yields are between 3 and 5% approximately, can also be observed. The intensity of the $m/z = 15$ amu/q (CH_3^+) signal is always higher than the intensities of the remainder ions of this group.

Other important contributing ions are CH_3S^+ and ClCO^+ . Both ions can be formed by the simple rupture of the C–S bond involving the carbonyl carbon atom, that could be understood as caused by electronic excitations from inner shell levels to the vacant $\sigma^*_{\text{C-S}}$ orbital, which is known to play a relevant role in the electronic spectra of $\text{CH}_3\text{C(O)SH}$.⁴

Other less abundant ions are the following: CH_xS^+ ($x = 0, 2$) with $m/z = 44$ and 46, OCS^+ ($m/z = 60$), and O^+/S^{2+} ($m/z = 16$). A signal for the H_2^+ ion also appears in these spectra, having weak relative intensity (1% approximately). This fragment is a typical signature of processes relating rearrange-

Table 1. Branching Ratios (%) for Fragment Ions Extracted from PEPICO Spectra Taken at Photon Energies around the S 2p, Cl 2p, C 1s, and O 1s Energies for ClC(O)SCH₃

electronic edge	photon energy (eV)	branching ratios at various <i>m/z</i> values (amu/q)																				
		1 H ⁺	2 H ₂ ⁺	12 C ⁺	13 CH ⁺	14 CH ₂ ⁺	15 CH ₃ ⁺	16 O ⁺ /S ²⁺	17.5 Cl ²⁺	28 CO ⁺	32 S ⁺	33 SH ⁺	35 Cl ⁺	44 CS ⁺	45 HCS ⁺	46 H ₂ CS ⁺	47 H ₃ CS ⁺	60 OCS ⁺	63 ClCO ⁺	67 ClS ⁺	75 COSCH ₃ ⁺	110 M ⁺
S 2p	164.8	5.3	1.2	4.1	4.0	5.4	8.8	2.9		6.4	6.8	1.8	7.1	3.3	9.2	2.8	4.8	3.2	4.9	2.5	5.7	2.2
	165.9	6.8	1.2	3.9	3.8	5.7	8.9	3.0		5.3	6.9	2.0	7.4	3.6	10.0	3.4	4.4	2.7	4.6	2.2	5.6	1.7
	167.1	8.8	1.0	3.5	3.6	5.4	8.2	2.1		5.3	6.8	1.7	7.9	4.0	12.0	3.7	4.4	2.0	4.6	1.4	6.1	1.3
Cl 2p	172.0	8.1	1.4	3.7	3.6	5.2	9.2	2.7		6.9	6.1	1.7	7.8	3.8	9.2	2.6	4.1	2.5	7.0	1.6	4.1	1.5
	199.4	11.0	1.5	4.4	4.1	5.8	8.8	2.4		6.9	7.3	1.6	9.2	3.0	8.8	2.4	3.7	2.0	5.8	1.2	2.7	1.1
	201.6	12.0	1.4	4.4	4.1	6.0	9.1	2.3		6.9	7.8	1.5	9.5	3.0	8.8	2.3	3.6	1.8	5.6	1.0	2.4	0.7
C 1s	209.0	12.0	1.3	4.1	3.8	5.8	11.0	2.2		7.0	7.4	1.5	11.0	2.7	7.9	2.1	3.4	2.5	4.6	0.9	2.2	0.6
	285.3	23.0	1.7	6.1	4.9	7.1	10.0	3.2	0.6	5.4	8.3		8.1	1.3	7.9		3.6	1.0	1.7		0.8	
	288.7	21.0	1.6	6.4	5.0	6.6	7.8	3.7	1.1	6.5	7.7		9.9	1.5	6.7		3.4	1.3	2.5		1.1	
O 1s	289.6	22.0	1.5	6.5	4.9	6.4	8.1	3.6	0.9	6.6	8.0		11.0	1.5	6.3		2.9	1.1	2.5		0.8	
	290.7	21.0	1.5	6.5	4.8	6.3	8.1	3.7	0.9	6.6	8.0		11.0	1.5	6.2		3.0	1.2	2.4		0.9	
	291.7	22.0	1.6	6.6	4.9	6.4	8.2	3.9	0.9	6.6	8.1		11.0	1.3	6.0		2.9	1.1	2.3		0.8	
	292.8	23.0	1.6	6.5	4.9	6.5	8.2	3.7	0.8	6.5	7.9		11.0	1.5	6.1		2.7	1.1	2.3		0.7	
	297.0	22.0	1.6	6.3	4.9	6.6	8.3	3.6	0.9	6.5	7.9		11.0	1.3	6.3		2.9	1.1	2.3		0.8	
	525.0	28.0	1.5	7.8	4.7	5.7	6.7	4.7	0.9	5.8	7.8		10.0	1.2	4.3		2.0	0.8	1.6		0.5	
	532.8	26.0	1.6	7.5	4.8	5.8	6.5	4.8	1.2	5.7	7.5		9.5	1.5	4.7		2.5	1.1	1.9		0.9	
	536.0	26.0	1.5	7.8	4.7	5.6	6.4	5.0	1.2	5.9	7.8		10.0	1.3	4.5		2.4	1.1	1.9		0.8	
	545.0	28.0	1.5	7.7	4.7	5.8	6.7	4.9	0.9	5.8	7.7		10.0	1.2	4.6		2.1	0.8	1.7		0.5	

^aPeaks for the corresponding naturally occurring isotopomer were observed.

ment reactions.⁴² In addition, the SH^+ and ClS^+ ions could be observed in the PEPICO spectra and also involve rearrangement reactions.

The analysis of the PEPICO spectra of FC(O)SCH_3 following S 2p, C 1s, O 1s, and F 1s inner shell excitations also was revealed a preferential production of HCS^+ ions, while signals corresponding to ionic fragments CS^+ and H_2CS^+ also appear as less intense bands. This ion has been also constantly observed in the ionic fragmentation of other sulfur compounds having a methyl group as CH_3SCN ,⁴³ $\text{ClC(O)SCH}_2\text{CH}_3$,⁷ and $\text{CH}_3\text{C(O)SCH}_3$.

The thioformyl ion HCS^+ is not only one of the more than 140 species recognized in the interstellar medium up to date but one of the key species to understand the interstellar sulfur chemistry. As we mentioned in a previously reported article,⁶ its $\text{C}=\text{S}$ bond is extremely strong and the abundance ratio HCS^+/CS^+ observed in the interstellar medium was found to be unusually higher than those predicted by theoretical computations.^{44–47} This is due to its low recombination energy (charge transfer reactions are inhibited therefore) and the relatively large proton affinity of CS, which inhibits proton transfer from HCS^+ to most molecular species. Thus, HCS^+ is rather unreactive with all of the most abundant interstellar molecules and consequently an important factor for its abundance in interstellar clouds.^{48,49}

Other important contribution to the PEPICO spectra is the C(O)SCH_3^+ ($m/z = 75$ amu/q), the heaviest fragment detected in the PEPICO spectra, with relative abundances between 4.1 and 6.1% in the S 2p region. This signal is assigned to the loss of a Cl atom from the parent molecular ion ($M^+ - 35$). Only a singly charged molecular ion can produce the signal of C(O)SCH_3^+ observed in the spectra.

In addition, signals of OCS^+ , ClCO^+ , and ClS^+ fragments could also be produced only from the singly charged species ClC(O)SCH_3^+ . In effect, even the whole remaining ClCH_3 , SCH_3 , and COCH_3 groups are lighter than the OCS, ClCO, and ClS ones and should be detected in the PEPICO spectra instead of OCS^+ , ClCO^+ , and ClS^+ if the multiple ionization processes occurs.

The parent ion, ClC(O)SCH_3^+ , can be observed at $m/z = 110$ amu/q in all PEPICO spectra recorded at selected energies around the S 2p and Cl 2p absorption edges having relative intensities between 2.2 and 1% in the TOF mass spectra measured at photon energies near the S 2p and lower than 1% around the Cl 2p region. This ion shows the isotopomeric characteristics due to the chlorine isotopic normal abundance.

An enhancement in the intensities of the signals corresponding to the ions H^+ and Cl^+ can be noticed by going from the S 2p to the Cl 2p region, having their relative intensities higher than the HCS^+ ion. Furthermore, a diminution in the intensity of the C(O)SCH_3^+ ion signal is evident when the incident photon energy is increased.

However, the intensity value of the atomic hydrogen ion represents the highest in all energy range around the C 1s edge, which possess relative abundance higher than 20%. The next most important ions with relative intensities between 7.7% and 11% are CH_3^+ , S^+ , and Cl^+ . The thioformyl species formerly observed near the S 2p edge as the most important ion reveals at this high energy range (C 1s), an intensity value of 6% approximately.

New weak intensity signals (1% approximately) appear at $m/z = 17.5$ and 18.5 amu/q and correspond to double charged chlorine isotopes. The formation of doubly charged ions

suggests the presence of dissociation channels involving the production of the dication and a neutral species or the occurrence of triple ionization processes. Coincidentally, with the observed atomization processes, the molecular ion cannot be observed at these high energies.

Signals at 75 (C(O)SCH_3^+) and 63 (ClCO^+) amu/q decrease when the photon energy is increased (Figures 3 and 4), whereas the signal located at 67 (ClS^+) amu/q vanishes completely when the incident photon energy is increased (see Figure 3 with selected photon energies around the S 2p and Cl 2p edge absorptions). Thus, at this high relative photon energy region, processes involving singly charged ions are, as expected, less important than the doubly charged ion channels.

However, the fragmentation patterns at the C and O 1s edges seem to be basically similar. That is, the H^+ ion is once more the most abundant fragment, formed with relative abundances between 26 and 28%, and the next most abundant ions are Cl^+ and S^+ , respectively.

Near the O 1s edge, the intensity of the C^+ ion (7.5% approximately) is always higher than the intensity of the methyl fragments CH_x^+ ($x = 1, 2, 3$) evidencing a different behavior than that observed in the S 2p, Cl 2p, and C 1s regions, where the abundance of the CH_3^+ ion is always higher than the intensities of the remainder ions of this group.

The analysis of the PEPICO spectra of ClC(O)SCH_3 over the whole range of photon energies analyzed here reveals that the atomization processes become dominant when the photon energy is increased. Thus, a clear enhancement in the intensity of the signal corresponding to the ion H^+ can be observed, from 5.3% near the S 2p edge to 28% near the O 1s edge. In addition, an increase in the peak intensities, corresponding to the atomic ions C^+ , O^+/S^{2+} , S^+ , and Cl^+ become apparent by going toward higher energies. However, intensity peaks corresponding to ionic fragments such as HCS^+ , ClCO^+ , and C(O)SCH_3^+ are weaker approximately from 12.0 to 4.3%, 7.0 to 1.6%, and 6.1 to less than 1% by going from the S 2p to the O 1s region. These evidence can be related with the occurrence of a moderate site-specific fragmentation in ClC(O)SCH_3 . For the sake of comparison, Figure 5 shows the PEPICO spectra of ClC(O)SCH_3 obtained at resonant S 2p, C 1s, and O 1s energies.

It is also important to notice that the $[M - 28]^+$ ion is absent in the photon-excited PEPICO spectra of ClC(O)SCH_3 over

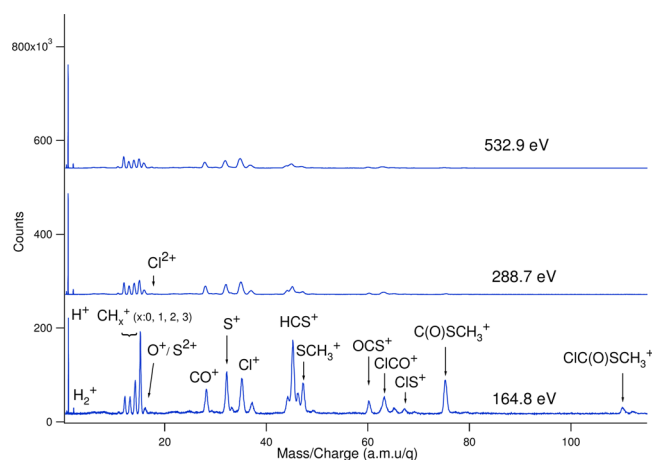


Figure 5. PEPICO spectra of ClC(O)SCH_3 at resonant S 2p (bottom), C 1s (middle), and O 1s (top) edge absorptions.

Table 2. Relative Intensities for Double Coincidence Islands Derived from the PEPICO Spectra of ClC(O)SCH₃ As a Function of the Photon Energy

coincidences		partial double coincidence yield (PDCY) %							
ion 1	ion 2	164.8	172.0	199.4	209.9	288.7	297.0	532.9	545.0
H ⁺	C ⁺	8.4	7.2	8.2	12.4	21.2	26.9	22.2	29.5
H ⁺	CH ⁺	4.2	3.5	4.0	4.7	6.2	10.3	8.3	8.3
H ⁺	CH ₂ ⁺	2.5	1.4	2.1	2.2	3.1	4.4	4.4	3.6
H ⁺	O ⁺ /S ²⁺	1.0	1.0	1.2	1.5	10.1	10.0	8.9	13.9
H ⁺	CO ⁺	4.0	3.8	4.2	4.2	4.8	7.7	6.9	5.7
H ⁺	S ⁺	9.0	7.7	8.7	11.6	11.6	16.1	14.1	15.5
H ⁺	³⁵ Cl ⁺	6.8	6.2	6.7	10.3	5.3	8.0	6.9	6.5
H ⁺	CS ⁺	5.3		4.3	4.1	1.9	3.1	2.2	2.2
H ⁺	HCS ⁺	5.9	14.6	7.8	8.6	3.7	7.1	7.4	4.6
C ⁺	O ⁺ /S ²⁺					2.6		1.2	2.3
C ⁺	S ⁺	1.5		1.3		1.8		1.3	1.3
CH ⁺	S ⁺	2.1	1.2	1.6	3.0	1.1		1.2	0.7
CH ⁺	³⁵ Cl ⁺	1.3			1.6				
CH ₂ ⁺	S ⁺	5.4	3.0	3.4		1.5	1.4	1.8	1.0
CH ₂ ⁺	³⁵ Cl ⁺	2.7	2.0	1.8					
CH ₃ ⁺	CO ⁺	1.6		1.8					
CH ₃ ⁺	S ⁺	8.3	4.4	4.2	4.7	1.2	1.4	1.7	0.7
CH ₃ ⁺	³⁵ Cl ⁺	5.1	3.1	2.6	4.3				
CH ₃ ⁺	OCS ⁺	4.4	6.0	2.8	10.6				
CH ₃ ⁺	ClCO ⁺	2.0	7.2	3.4	2.4				
CO ⁺	S ⁺			1.1					
CO ⁺	HCS ⁺	2.7	3.8	2.7	2.4				
S ⁺	³⁵ Cl ⁺	2.1	1.5	2.5	2.6	2.1	1.8	1.8	1.4
³⁵ Cl ⁺	HCS ⁺	6.1		5.5	5.1				
HCS ⁺	³⁵ ClCO ⁺	2.5	12.4	5.9	2.9				
H ₃ CS ⁺	³⁵ ClCO ⁺		2.7						

the whole range of photon energies analyzed here. As we mentioned in the previously reported study of the title molecule in the valence-shell region, the $[M - 28]^+$ ion was neither observed. In the same way, the peak originated from the CO extrusion was not observed either in the PEPICO spectra of the ClC(O)SCH₂CH₃ molecule recently reported.⁸ However, the CO extrusion is clearly observed in the UV photolysis of matrix-isolated ClC(O)SCH₃, where CO and ClSCH₃ are the main products observed by infrared spectroscopy.⁵⁰ Flammang, Nguyen, and collaborators have studied the unimolecular chemistry of a series of S-alkyl thioformate radical cations, HC(O)SR^{•+}, radical cations.^{51,52} Decarbonylation of the molecular ions is a common process, and the $[M - 28]^+$ ion is readily observed by using tandem mass spectrometry methodologies. For HC(O)SCH₃, the proposed mechanism consists of a 1,2-hydrogen shift giving rise to the formation of a sulfurane intermediate ion.⁵³ It is possible that the migration of heavy atoms such as chlorine disfavors the formation of the sulfurane ion, and for that reason, the $[M - 28]^+$ ion is absent in the PEPICO spectra.

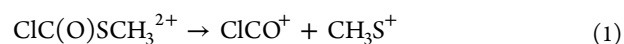
At this point, it becomes also interesting to compare the photon-excited dissociation of the related species ClC(O)SCH₃ and CH₃C(O)SCH₃. Indeed, strong differences are observed in the PEPICO spectra. For instance, whereas the OCSCH₃⁺ ion is predominantly formed from the title species, it is completely absent in the PEPICO spectra of CH₃C(O)SCH₃.

PEPIPO Spectra. The double coincidence branching ratio for double ion processes calculated from PEPICO spectra at several photon energies around S 2p, Cl 2p, C 1s, and O 1s ionization edges is given in Table 2.

As much as 47% of the double coincidences that originated from ClC(O)SCH₃ have the H⁺ ion as the lightest ion in the spectra recorded at 164.8, 172.0, and 199.4 eV. This contribution increases at approximately 60% when the photon energy is increased at 209.0 eV. Between others, the H⁺/CH_x⁺ ($x = 0, 1, 2$), H⁺/CO⁺, H⁺/S⁺, and H⁺/Cl⁺ are some of the more intense coincidences.

As also noted in the PEPICO spectra of the related molecule FC(O)SCH₃, it is also significant to observe the contribution of the HCS⁺ ion to the double coincidence spectra measured when photons impact gaseous ClC(O)SCH₃. Thus, the islands related to this fragment, which is known to possess a high thermodynamic stability, are observed at all the photon energies near the S 2p and Cl 2p edges studied with larger relative intensity than the double coincidence concerning the other ions corresponding to the series CH_xS⁺ ($x = 0, 2, 3$) some of which are observed with a relative abundance lower than 1.0%. The coincidences observed in the S 2p and Cl 2p regions involving the arrival of HCS⁺ ions as either the lightest or heaviest ion are H⁺/HCS⁺, Cl⁺/HCS⁺, CO⁺/HCS⁺, and HCS⁺/ClCO⁺.

Fragmentation processes leading to the formation of ClCO⁺ and SCH₃⁺ ions concerning with the rupture of the S–C (carbonylic carbon atom) bond were observed with the highest intensity (2.7%) at the S 2p threshold. The experimental parallelogram-like shape and the slope displayed by this coincidence with a value close to -1.0 can be explained by a two-body mechanism



The coincidence island for these two fragments is shown in Figure 6.

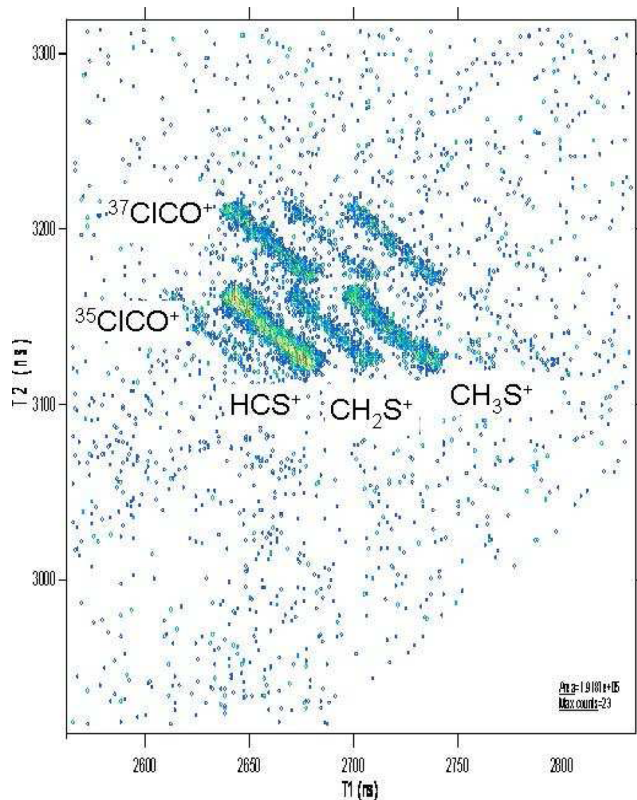
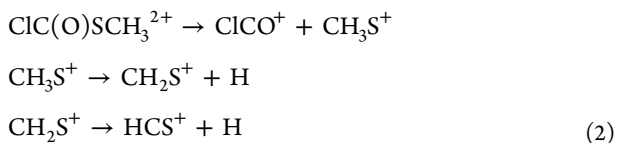


Figure 6. Enlargement of the PEPICO spectrum of ClC(O)SCH_3 obtained at 172.0 eV photon energy in the ranges of m/z 45–47 and 63–65 amu/q in the T1 and T2 domains, respectively.

Two-body processes concerning the rupture of the C–S bond to form two single-charged species were observed as the main two-body dissociation channel in double-charged XC(O)SY species excited at inner shell levels.

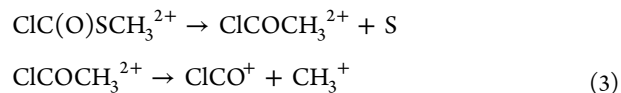
The contribution of the coincidence between ClCO^+ and HCS^+ ions to the double coincidence spectra was observed in the S 2p and Cl 2p regions, as mentioned before, with a maximum branching ratio of 12% at 172.2 eV. This pair of ions can be originated by assuming that the four-body secondary decay mechanism takes place, for which the calculated slope is -0.96 , in very good agreement with the experimental value of -0.94 (Figure 6).

As before discussed, the CH_3S^+ ion is formed in a first step by the rupture of the S–C (carbonylic carbon atom) bond, undergoes further dissociation processes involving the loss of neutral hydrogen atoms to give the HCS^+ fragment:

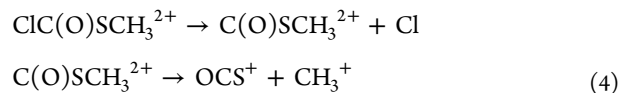


It is plausible that the high stability of HCS^+ favored the dissociation of the CH_3S^+ fragment. As both mechanisms 1 and 2 are clearly related, the low yield observed for the two-body fragmentation 1 can be associated with the dissociation of the CH_3S^+ ion toward HCS^+ .

A coincidence between CH_3^+ and ClCO^+ ions was also observed in the ClC(O)SCH_3 PEPICO spectra measured with a relative abundances between 2 and 7% at photon energies near the S 2p and Cl 2p edges. The experimental shape and the observed slope of -1.2 for this coincidence are better interpreted by the occurrence of the following three-body dissociation process in a deferred charge separation (DCS) scheme:



The observed slope for the $\text{CH}_3^+/\text{OCS}^+$, that is approximately -1 , can be explained by the following three-body ion pair process DCS:



As mentioned before, the C(O)SCH_3^+ ion could be produced from the singly charged species ClC(O)SCH_3^+ (Figure 3 and Table 1) and also could derive from doubly charged species. Thus, a coincidence between C(O)SCH_3^+ and Cl^+ ions is identified in the PEPICO spectra as an island with a cigar shape having a -1 slope in good agreement with the following two-body fragmentation process (Figure 7):

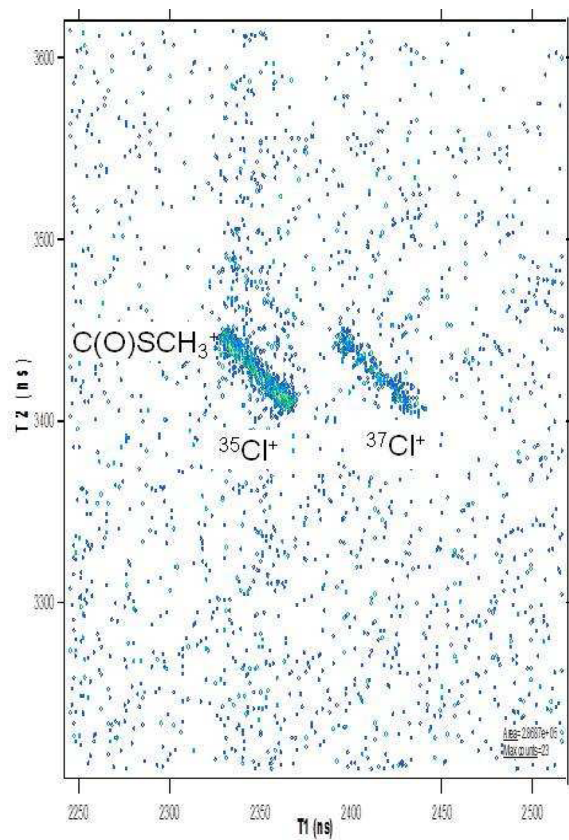
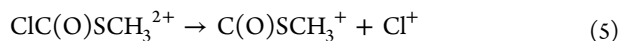


Figure 7. Enlargement of the PEPICO spectrum of ClC(O)SCH_3 obtained at 172.0 eV photon energy in the ranges of m/z 35–37 amu/q and 75 in the T1 and T2 domains, respectively.

However, the number of islands in the PEPICO spectra is lowered by going from the S 2p to the O 1s region.

As much as 70% of the double coincidences originating from ClC(O)SCH₃ have the H⁺ ion as the lightest ion in the spectrum obtained at 288.7 eV, in the C 1s region. This contribution increases when the photon energy is increased, accounting for 90% at 545.0 eV, in the O 1s region.

A clear enhancement in the intensity of the H⁺/C⁺ and H⁺/O⁺, S²⁺ coincidences is evident when the C 1s and O 1s edges are reached, having relative intensities higher than 20% and 10%, respectively. In addition, a diminution of the intensity of the double coincidence involving the molecular fragment CH₃⁺ with the S⁺ ion is observed from approximately 8% near the S 2p edge to around 1% near the O 1s edge.

The double coincidence involving the two heaviest fragments in both T1 and T2 domains correspond to the S⁺/Cl⁺ pair of ions, which possess relative abundances of approximately 2% in the C 1s and O 1s regions. At these high energies, the analysis of PEPICO spectra reveals the presence of a unique island involving the HCS⁺ ions. This island involves the arrival of this species as the heavier ion in coincidence with the H⁺ ion as the lighter fragment.

CONCLUSIONS

A series of well-structured resonant electronic transitions is observed in the TIY spectra of ClC(O)SCH₃ below the S 2p, Cl 2p, C 1s, and O 1s thresholds in the VUV and soft X-ray energy regions.

The most intense PEPICO peak for the S 2p energy range corresponds to the HCS⁺ ion. CH₃S⁺ and ClCO⁺ ions formed by the C–S rupture also derive from an important process. The heaviest fragment detected under this condition is C(O)SCH₃⁺, which must come from the ionized molecular ion. The parent ion, ClC(O)SCH₃⁺, can be observed in all PEPICO spectra recorded at selected energies around the S 2p and Cl 2p absorption edges. Atomization processes became apparent at higher energies. The intensity value of the atomic hydrogen ion represents the highest in all energy range around the C 1s edge. As expected, the fragmentation patterns at the C and O 1s edges seem to be basically similar. The [M – 28]⁺ ion is absent in the photon-excited PEPICO spectra of the title molecule over the whole range of photon energies used.

The contribution of HCS⁺ in the PEPICO spectra is also significant. PEPICO islands corresponding to H⁺/HCS⁺, Cl⁺/HCS⁺, CO⁺/HCS⁺, and HCS⁺/ClCO⁺ fragments are readily observed near the S 2p and Cl 2p edges. The two-body process rupture concerning the rupture of the S–C bond together with the subsequent formation of the ClCO⁺ and SCH₃⁺ ions can be observed near the S 2p threshold. However, the multibody dissociation of SCH₃⁺ toward HCS⁺ seems to be a very favored process. As expected, the number of PEPICO islands decreases with the increase of atomization processes at higher energies. It is important to remark that, at these high energies, the only nonatomic contribution is due to the HCS⁺ ions, which arrive to the detector in coincidence with the lighter H⁺ ion.

As already reported, the HCS⁺ ion plays an important role in the interstellar medium and constitutes a key species to analyze the interstellar sulfur chemistry. In our experiments, we observed also the presence of H₂⁺, whereas no evidence of the existence of H₃⁺ have been noted. This fact may be a consequence of kinetically controlled reactions. Thermody-

namically, the reaction of H₂⁺ with H₂, to mention only an example, would lead to H₃⁺ immediately.

As pointed out in our previous reported work, the interstellar dust plays an important role and, in some cases, may be preponderant to understand interstellar reactions. Another important difference when laboratory experiments and universe reactions are compared is that the universe possesses several orders of magnitude more time than our experiments. Nevertheless and also taken into account these facts, chemistry can be used in all sceneries.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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